

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: 23.01.91

71 Application number: 86109416.7

72 Date of filing: 10.07.86

86 Divisional application 89122521.1 filed on 10/06/86.

61 Int. Cl.⁵: **C 08 F 214/26, C 08 L 27/18 //**
(C08F214/26, 210:02, 216:14, 220:42)

54 **Fluorelastomers.**

30 Priority: 12.07.85 US 754499
11.12.85 US 807611
17.06.86 US 873165

43 Date of publication of application:
14.01.87 Bulletin 87/03

45 Publication of the grant of the patent:
23.01.91 Bulletin 91/04

14 Designated Contracting States:
DE FR GB IT NL

56 References cited:
EP-A-0 011 853
US-A-3 467 638

73 Proprietor: **E.I. DU PONT DE NEMOURS AND COMPANY**
1007 Market Street
Wilmington Delaware 19898 (US)

72 Inventor: **Ojakaar, Leo**
8 Jacqueline Driver
Hockessin, DE 19707 (US)
Inventor: **Moore, Albert Lloyd**
2213 Old Orchard Road
Wilmington, DE 19810 (US)

74 Representative: **von Kreisler, Alek, Dipl.-Chem. et al**
Deichmannhaus am Hauptbahnhof
D-5000 Köln 1 (DE)

EP 0 208 314 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

BEST AVAILABLE COPY

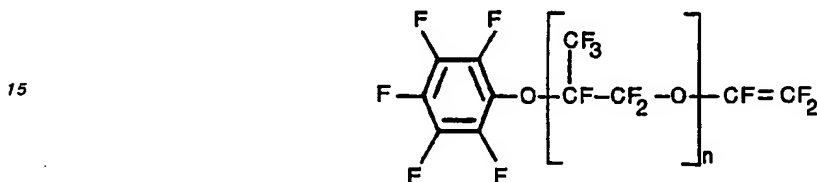
EP 0 208 314 B1

Description

This invention relates to substantially amorphous fluoroelastomers resistant to attack by amines, strong bases and hydrogen sulfide and, at the same time, the fluoroelastomers possess a combination of good low temperature and high temperature properties and they are resistant to oil swell.

EP—A—0 011 853 discloses vulcanizable copolymers of tetrafluoroethylene, perfluoromethyl perfluorovinyl ether and a cyano-substituted perfluorovinyl ether such as perfluoro-(8-cyano-6-methyl-3,6-dioxa-1-octene) and perfluoro-(9-cyano-5-methyl-3,6-dioxa-1-nonene) and elastomeric vulcanizates thereof.

US—A—3 467 638 discloses the copolymerization of monomers of the formula



where n is 1 or 2, with other vinyl-type monomers such as perfluoromethyl perfluorovinyl ether and tetrafluoroethylene.

Vinylidene fluoride-based polymers, such as copolymers of vinylidene fluoride and hexafluoropropylene, optionally containing tetrafluoroethylene, have achieved outstanding commercial success. However, in certain applications in which these fluoroelastomers are in contact with amines or strong bases at high temperatures, the fluoroelastomers are attacked by these materials and they lose their elastomeric characteristics principally by becoming hard and brittle. Such is the case when vinylidene fluoride-based fluoroelastomers are used as seals in oil drilling operations where the fluoroelastomer is exposed to a combination of both high and low temperatures, amines and hydrogen sulfide, all of which are associated with oil well drilling environments. Other fluoroelastomers that are known to be resistant to attack by amines, such as copolymers of tetrafluoroethylene/propylene, cannot be used successfully where long term resistance to low temperature is required because these copolymers lose their flexibility at low temperatures and, further, since these fluoroelastomers contain a relatively large amount of propylene, they tend to swell in the presence of oil and, consequently increase in size.

Fluoroelastomers that contain ethylene and perfluorovinyl ethers at a molar ratio of ethylene to perfluorovinyl ether of 95:5 to 30:70 where the total content of ethylene plus perfluorovinyl ether is at least 70 mole percent are difficult to prepare commercially because the combination of ethylene and perfluorovinyl ether is not readily polymerizable to sufficiently high molecular weights and, additionally, high levels of expensive perfluorovinyl ether monomer must be used to attain a satisfactory fluorine content.

In the case of copolymers of ethylene/tetrafluoroethylene/perfluoro(alkyl vinyl ether)/cure-site monomer of the present invention having levels of 32—60 mole percent tetrafluoroethylene units, polymerization occurs more readily because of the reactivity of the tetrafluoroethylene monomer and high molecular weight fluoroelastomers are easily obtained. The high level of tetrafluoroethylene units incorporated in the fluoroelastomer gives the desired high level of fluorine in the polymer with only moderate amounts of the expensive perfluoro(alkyl vinyl ether).

Vinylidene fluoride-based fluoroelastomers which do not contain a cure-site monomer can be cured by conventional techniques by employing crosslinking agents such as diamines and bisphenols. However, the fluoroelastomers of the present invention that have a base-resistant polymer backbone cannot be cured in a practical manner by conventional techniques mentioned above, unless a cure-site monomer is incorporated in the polymer.

The substantially amorphous fluoroelastomers of the present invention have good low temperature properties since they have glass transition temperatures of -10°C or below, while at the same time, the fluoroelastomers are especially resistant to swelling when in contact with oil. Furthermore, the fluoroelastomers of the present invention have excellent high temperature properties, solvent resistance and, most importantly, they are resistant to attack by strong base and amines.

Summary of the Invention

The present invention is directed to a base resistant, substantially amorphous fluoroelastomer consisting of (1) 10—40 mole percent ethylene units, preferably 20—40 mole percent, (2) 32—60 mole percent tetrafluoroethylene units, (3) 20—40 mole percent perfluoro(alkyl vinyl ether) units, preferably 20—35 mole percent, wherein the alkyl group contains 1—5 carbon atoms and (4) a cure-site monomer. Depending on the type of cure-site monomer present the fluoroelastomers can be cured by free radical procedures, i.e., peroxide cures or chemical crosslinking reactions, e.g., diamine cures or bisphenol cures. Preferably, peroxide curable cure-site monomers; especially bromine containing olefins having 2—20 carbon atoms are incorporated in the polymers.

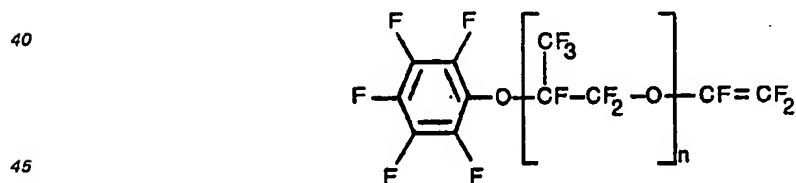
The amorphous fluoroelastomers are especially useful for the manufacture of O-rings or shaft seals used, for example, in oil drilling apparatus where the elastomeric seals employed in such hostile environments must have long-term resistance at both low temperatures and high temperature in aqueous or organic fluids containing strong base, amines or hydrogen sulfide.

5 The resulting cured tetrafluoroethylene-containing fluoroc elastomer compositions of the present invention can be used to make articles such as O-rings, hose, gaskets, shaft seals and the like.

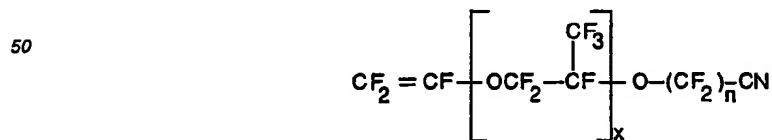
Description of Preferred Embodiments

The fluoroelastomers of the present invention must contain 10—40 mole percent ethylene units, preferably 20—40 mole percent, 32—60 mole percent tetrafluoroethylene units, and 20—40 mole percent perfluoro(alkyl vinyl ether) units, preferably 20—35 mole percent and up to 3 mole percent of a cure-site monomer. The perfluoro(alkyl vinyl ethers) that can be used in this invention usually contain alkyl groups having 1—5 carbon atoms, preferably 1—3 carbon atoms, and most preferably the perfluoro(alkyl vinyl ether) is perfluoro(methyl vinyl ether) because it is more readily polymerizable to allow preparation of high molecular weight fluoroelastomers. Representative perfluoro(alkyl vinyl ethers) include perfluoro(methyl vinyl ether), perfluoro(ethyl vinyl ether), perfluoro(propyl vinyl ether), perfluoro(butyl vinyl ether), perfluoro(pentyl vinyl ether). To obtain fluoroelastomers with lower glass transition temperatures, up to 5 mole percent of the perfluoro(alkyl vinyl ether) units can be replaced with perfluoro(alkoxy alkyl vinyl ether) units and, therefore, the term "perfluoro(alkyl vinyl ether)" as used herein is intended to include those monomers that also contain minor amounts of up to 5 mole percent of perfluoro(alkoxy alkyl vinyl ethers). Representative perfluoro(alkoxy alkyl vinyl ethers) wherein the alkoxy and alkyl groups each contain 1—5 carbon atoms that can be used in this invention include perfluoro-(2-n-propoxypropyl vinyl ether), perfluoro(3-methoxy-propyl vinyl ether), perfluoro(2-methoxypropyl vinyl ether) and perfluoro(2-methoxyethyl vinyl ether). If the fluoroelastomers of this invention contain more than 40 mole percent ethylene or less than 20 mole percent perfluoro(alkyl vinyl ether) then they are unsatisfactory because the fluoroelastomers are not sufficiently amorphous. If the fluoroelastomer contains more than 3 mole percent the cure-site monomer, polymerization to the desired high molecular weight is difficult and the vulcanizate crosslinked density is too high for practical use as an elastomer. The fluoroelastomers of the present invention have good low temperature properties, i.e., the fluoroelastomers have glass transition temperatures (T_g), measured by a Differential Scanning Calorimeter in the heating mode at the onset of transition, of -10°C or below, generally within a range of -10 to -20°C.

The fluoroelastomers of the present invention contain a cure-site monomer. The cure-site monomer is present in the fluoroelastomer in amounts up to 3 mole percent. Generally, at least 0.2 mole percent of cure-site monomer is present in the fluoroelastomer and, usually, not more than 2 mole percent is required to be present in the fluoroelastomer. Various cure-site monomers can be incorporated into the backbone of the fluoroelastomer. Representative cure-site monomers include brominated or iodinated alpha-olefins containing 2—20 carbon atoms, or halogenated vinyl ethers, of the formulae:



where n is 1 or 2,



55 where n is 1 to 4, and X is 1 to 2,

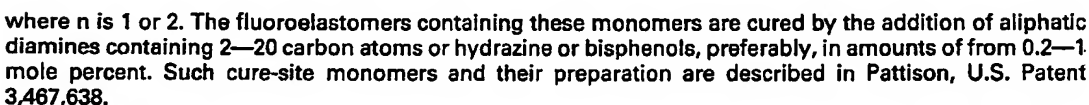


60 where Y is chlorine, bromine or iodine, X is hydrogen or fluoride and n is 1 to 9. Preferably, the cure-site monomer is one that imparts peroxide curability to the fluoroelastomer, such as bromine-containing olefins or iodine-containing olefins. Peroxide-curable fluoroelastomers are preferred because of the enhanced hydrolytic stability of the vulcanizate.

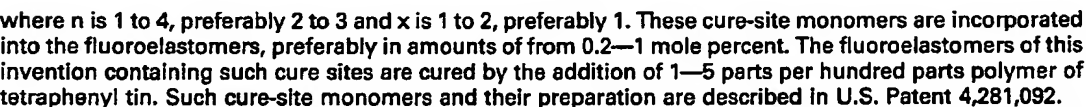
The term "bromine-containing olefin" or "iodine-containing olefin" as used herein means an olefin in which at least one hydrogen atom has been replaced with a bromine atom or an iodine atom, respectively,

and optionally, one or more of the remaining hydrogen atoms have been replaced with an atom of another halogen, preferably fluorine. Some compounds of this type are available commercially and others can be prepared by methods known in the art, for example, as shown by Tarrant and Tandon, *J. Org. Chem.* **34**, 864 (1969) and by Fainberg and Miller, *79 JACS* 4170 (1957) and *J. Org. Chem.* **42** 1985—90 (1977).

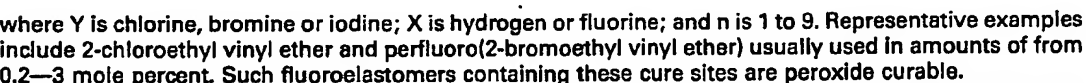
Additional cure-site monomers that can be incorporated in the fluoroelastomers described herein are represented by the formula:



Other representative cure-site monomers that can be incorporated into the fluoroelastomers of the present invention have the formula:



Other compounds useful as cure-site monomers for the fluoroelastomers of this invention are represented by the formula:



The fluoroelastomers of this invention are prepared by polymerizing ethylene, tetrafluoroethylene, perfluoroalkyl perfluorovinyl ether, and a cure-site monomer, by emulsion processes in which all the monomers are continuously added to the reactor in much the same manner, and under substantially the same conditions, as described in Apotheke et al., U.S. Patent 4,035,565, especially Example 1. For further details on such emulsion polymerization processes see also Moore, U.S. Patent 3,839,305 and Gladding et al., U.S. Patent 3,707,529.

More specifically, in preparing the fluoroelastomer to be used in the present invention, it is preferred that the reaction mixture of monomer components also contains a free-radical initiator, and the polymer-forming reaction is carried out as a free-radical emulsion polymerization reaction. Among the most useful

free-radical initiators to use in such a reaction are ammonium persulfate, sodium persulfate, potassium persulfate, or a mixture of two or more such compounds. Also useful are other water-soluble inorganic peroxide compounds, for example, sodium, potassium, and ammonium perphosphates, perborates, and percarbonates. The initiator can be used in combination with a reducing agent such as sodium, potassium, or ammonium sulfite, bisulfite, metabisulfite, hyposulfite, thiosulfate, phosphite, or hypophosphite, or in combination with a ferrous, cuprous, or silver salt, or other easily oxidized metal compound. Known organic free-radical initiators can also be used in combination with a suitable surfactant such as ammonium perfluoro-octanoate. The surfactant can be selected from those known to be useful in the manufacture of fluoroelastomers. A surfactant is present when using an inorganic initiator. A buffer, such as disodium phosphate, can be added to control the pH within a range of 3—7. Optionally, a known chain transfer agent can be present during the emulsion polymerization reaction. Examples of such chain transfer agents include diiodomethane, isopropanol, diethyl malonate, methylene bromide.

After completion of the emulsion polymerization reaction, the fluoroelastomer can be isolated from the resulting polymer latex by known methods, for example, by coagulation by adding an electrolyte or by freezing, followed by centrifuging or filtering and then drying the fluoroelastomer.

The polymer-forming reaction can also be carried out in bulk, or in an organic liquid containing an organic free-radical initiator.

During preparation of the fluoroelastomer, the reaction mixture is preferably heated in a reactor which has been flushed with an inert gas at 40—130°C under superatmospheric pressure, for example, under a pressure of 0.7—14 MPa, preferably 3—10 MPa. In some of the most useful procedures, the polymerization is carried out as a continuous process and the reaction mixture has an average residence time in the reactor of 0.5 to 5 hours. Residence time can be calculated by dividing the reactor volume by the volume of latex produced per hour.

The fluoroelastomer in the majority of cases will have an inherent viscosity of 0.2 dl/g or higher, with special preference for an inherent viscosity of 0.3—1 dl/g. Inherent viscosities of the fluoroelastomers can be measured at 30°C at a fluoroelastomer concentration of 0.2% by weight in a solvent consisting of 60/40/3 volume ratio of heptafluoro-2,3,3-trichlorobutane, perfluoro(butyltetrafluorohydrofuran) and ethylene glycol dimethyl ether.

Optionally, at least one metal compound selected from divalent metal oxides or divalent metal hydroxides is frequently blended with the fluoroelastomer during preparation or before it is cured. These metal compounds absorb certain gases and acidic materials which are evolved during vulcanization that can chemically attack and weaken the fluoroelastomer. The presence of such compounds improves the heat aging resistance and thermal stability of the polymer. Representative metal compounds include the oxides and hydroxides of magnesium, zinc, calcium, or lead. A metal salt of a weak acid can be used along with the oxide and/or hydroxide. Representative metal salts of weak acids include barium-, sodium-, potassium-, lead- and calcium-/stearate, -benzoate, -carbonate, -oxalate and -phosphite. Lead oxide is especially preferred. The metal compound is added to the fluoroelastomer in an amount equal to 1—15%, preferably amount 2—10%, by weight of the fluoroelastomer.

When a peroxide is used as the curing agent, conventional coagents that are polyunsaturated compounds and cooperate with the peroxide curative to provide a useful cure can be added to the fluoroelastomer composition to increase its cure rate. The amount of coagent added to the composition is, generally, between 0.25—10, usually 0.5—5 parts per 100 parts fluoroelastomer. Representative coagents well known in the art that can be used in the invention are described in U.S. Patent No. 4,214,060. Especially effective coagents include triallyl isocyanurate, triallyl cyanurate, trivinyl isocyanurate and trimethallyl isocyanurate.

The fluoroelastomers can also contain conventional fillers such as carbon black, silica, clay and talc; other fillers, pigments, antioxidants, stabilizers can be used. It is particularly advantageous to add carbon black to the fluoroelastomer to increase its modulus. Usually amounts of from 5—50 parts per hundred parts fluoroelastomer are used with the particular amount determined from the particle size of the carbon black and the desired hardness of the cured composition.

The following examples illustrate preferred embodiments of the invention.

Example 1

A continuous emulsion polymerization was carried out in a well-stirred 2.0-liter stainless steel reaction vessel. The reactor was filled with an aqueous solution containing 2.2 g ammonium persulfate (APS) and 0.6 g sodium sulfite initiator components, 2.0 g ammonium perfluorooctanoate (FC-143) soap, and 10.0 g disodium hydrogen phosphate heptahydrate buffer per liter of deionized water. The reactor was heated to 90°C and the aqueous solution was fed at 1.00 liter/hour (solution was split into two streams, one containing APS and the other the remaining components). The reactor was kept liquid-full at 6.3 MPa by means of a back-pressure control valve in the effluent line. After one hour the polymerization reaction was started by introducing a gaseous monomer mixture of approximately 20 g/h ethylene, 110 g/h tetrafluoroethylene, and 150 g/h perfluoro(methyl vinyl ether) fed through a diaphragm compressor. After four hours, 4-bromo-3,3,4,4-tetrafluorobutene-1 was introduced to the reactor at a rate of approximately 3 g/h. After an equilibration period of two hours, the effluent polymer latex was collected for four hours.

The polymer latex was separated from residual monomers in a degassing vessel at atmospheric

EP 0 208 314 B1

pressure. The latex had a pH of 4.5 and contained about 15% solids. The fluoroelastomer was isolated from the latex by reducing the pH to about 3 with dilute nitric acid and coagulating with a calcium nitrate solution. The coagulated polymer was allowed to settle and was washed by reslurrying in water twice before filtering. The wet crumb was dried in an air oven at 50–60°C to a moisture content of less than 1%.

5 The fluoroelastomer had the following composition as determined by elemental analysis and ^{19}F nuclear magnetic resonance spectroscopy:

	Monomer	Wt %	Mole %
10	Ethylene	6	21
	Tetrafluoroethylene	51	53
	Perfluoro(methyl vinyl ether)	42	26
15	4-bromo-3,3,4,4-tetrafluorobutene-1	1.4	0.7

The glass transition temperature (T_g) was -18°C and crystallinity was negligible, as determined by differential scanning calorimetry (DSC) (heating mode, $10^\circ\text{C}/\text{min}$, onset of transition). The inherent viscosity of the fluoroelastomer was 0.51 dl/g, measured at 30°C at a polymer concentration of 0.2 g/dl in a solvent consisting of 60/40/3 volume ratio of heptafluoro-2,3,3-trichlorobutane, perfluoro(butyltetrahydrofuran) and ethylene glycol dimethyl ether. The Mooney viscosity of the fluoroelastomer measured as ML-10 (121°C) was 48.

A curable fluoroelastomer composition was prepared by mixing the following ingredients on a two-roll rubber mill whose rolls were heated to about 30°C : 100 parts fluoroelastomer of Example 1, 30 parts MT carbon black, 3 parts lead oxide (litharge), 3 parts triallyl isocyanurate, and 3 parts "Luperco®" 101-XL peroxide [45% of 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane and 55% inert filler]. Cure characteristics of the composition were measured with an oscillating disk rheometer (ODR) at a cure time of 12 minutes at 177°C , according to ASTM D-2084. The time required to reach 90% of the cure state reached in 12 minutes was determined at t_{90} was 6.0 minutes. Test samples were press-cured for 15 minutes at 177°C and post-cured in a circulating air oven for 24 hours at 232°C . Stress-strain properties were determined according to ASTM D-412 as: 100% modulus, $M_{100} = 4.8 \text{ MPa}$; tensile strength at break, $T_b = 10.0 \text{ MPa}$; elongation at break, $E_b = 220\%$. Good low-temperature flexibility was indicated by a Clash-Berg temperature of -9°C (temperature at which flex modulus reaches 10,000 psi or 69 MPa).

Example 2

A fluoroelastomer was prepared as described in Example 1, except as follows: The aqueous solution was fed at 0.80 L/h for a nominal residence time of 2.5 h in the 2.0-L reactor. The components of the aqueous solution were fed to the reactor at rates of 2.1 g/h ammonium persulfate, 10.0 g/h disodium phosphate buffer, and 0.8 g/h ammonium perfluorooctanoate soap. The gaseous monomers were fed to the reactor at rates of 20 g/h ethylene, 75 g/h tetrafluoroethylene, and 155 g/h perfluoro(methyl vinyl ether). The 4-bromo-3,3,4,4-tetrafluoro-butene-1 cure-site monomer was fed at a rate of 3.2 g/h. After equilibration for ten hours the latex was collected for sixteen hours. The unreacted offgas amounted to 57 g/h and had a composition of 0.0% ethylene, 13.5% tetrafluoroethylene and 86.5% perfluoro(methyl vinyl ether) as determined by gas chromatography. The polymerization rate was approximately 196 g/h at a conversion of 77%. The effluent latex had a pH of 3.9 and contained 19.0% solids.

The isolated fluoroelastomer had the following composition:

	Monomer	Wt %	Mole %
50	Ethylene	11	35
	Tetrafluoroethylene	35	33
55	Perfluoro(methyl vinyl ether)	54	32
	4-bromo-3,3,4,4-tetrafluorobutene-1	1	0.4

The inherent viscosity was 0.64 dl/g and the Mooney viscosity ML-10 (121°C) was 42. The glass transition temperature was -15°C and crystallinity was negligible.

One hundred parts of the fluoroelastomer described above was compounded on a two-roll rubber mill heated to about 30°C with 25 parts MT black, 5 parts calcium hydroxide, 5 parts triallyl isocyanurate (TAIC), and 3 parts Luperco® 101-XL peroxide. The cure characteristics of the composition were measured with an oscillating disc rheometer (ODR) for 30 minutes at 177°C according to ASTM D-2084 which indicated that optimum cure time t_{c90} was 4.3 minutes. Test samples were press-cured for 30 minutes at 177°C and

EP 0 208 314 B1

postcured for 24 hours at 200°C. Stress-strain properties according to ASTM D-412 were measured: $M_{100} = 9.0$ MPa, $T_B = 18.6$ MPa, and $E_B = 190\%$. A sample which was exposed to an aqueous solution of 50% sodium hydroxide and 0.2% quaternary amine salt for 3 days at 150°C retained reasonable stress-strain properties: $T_B = 7.4$ MPa, $E_B = 100\%$. A similarly exposed control vulcanizate of a commercial vinylidene fluoride-containing fluoroelastomer was reduced to tar.

Examples 3 to 6

Fluoroelastomers were made by continuous emulsion polymerization in a well-stirred 4.0-liter stainless steel reaction vessel, under the conditions described in Table I. In each run, the reactor was filled with an aqueous solution containing ammonium persulfate initiator, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ buffer, and ammonium perfluorooctanoate soap (FC-143). The reactor was heated to the desired operating temperature and goal feed rate of aqueous solution was established for one hour. The reactor was kept liquid-full at 6.3 MPa by means of a back-pressure control valve in the effluent line. The reaction was started by introducing a monomer gas mixture [ethylene, tetrafluoroethylene, and perfluoro(methyl vinyl ether)] fed through a diaphragm compressor. After 0.5 hour, 4-bromo-3,3,4,4-tetrafluorobutene-1 was introduced as a 50 volume % solution in tertiary-butanol. After a prescribed equilibration period, the effluent latex was collected as noted in the Table. The latex was degassed and the polymer was isolated as described in Example 1. The polymerization results and polymer characteristics are listed in Table I. All polymers were amorphous elastomers.

TABLE I

Example	3	4	5	6
Polymerization: Temperature, °C	90	90	100	100
Residence time, h	3.2	3.3	4.0	4.0
Aq. sol'n feed, L/h	1.25	1.20	1.00	1.00
Ammonium persulfate, g/h	2.7	3.0	1.6	1.6
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$, g/h	15	20	15	15
Ammonium perfluorooctanoate, g/h	1.5	3.2	2.7	2.7
Monomer feed g/h				
Ethylene	33	23	21	17
TFE ⁽¹⁾	126	198	131	138
PMVE ⁽²⁾	247	242	210	197
BTFB ⁽³⁾	8.1	6.2	5.3	5.2
Total	414	469	367	357
Run duration, h				
Equilibration Period	9	5	6	6
Collection	24	30	24	20
Offgas, g/h	122	113	99	99
Wt % Ethylene	0.1	0.0	0.1	0.0
TFE	14.2	16.6	14.7	16.0
PMVE	85.7	83.4	85.2	84.0

EP 0 208 314 B1

TABLE I (continued)

Example	3	4	5	6
Latex				
% Solids	18.8	23.7	21.9	21.2
pH	4.4	4.7	4.9	6.5
Polym'n rate, g/h	290	355	268	257
Conversion, %	70	76	73	72
Polymer: Composition				
Wt % Ethylene	11.4	8.4	7.8	6.7
TFE	37.2	50.5	43.6	47.4
PMVE	48.9	41.5	46.9	44.0
BTFB	2.5	1.6	1.7	1.9
Mole % Ethylene	37.4	22.9	27.7	24.1
TFE	34.3	51.0	43.3	48.1
PMVE	27.2	25.3	28.2	26.9
BTFB	1.1	0.8	0.8	0.9
Viscosity				
Inherent Visc., dL/g	0.59	0.48	0.54	0.72
ML-10 (100°C)		56	60	85
ML-10 (121°C)	40	29	36	56
DSC				
Tg°C	-12	13	16	18

- (1) TFE is tetrafluoroethylene
(2) PMVE is perfluoro(methyl vinyl ether)
(3) BTFB is 4-bromo-3,3,4,4-tetrafluorobutene-1

EP 0 208 314 B1

TABLE II
Curing of Compositions of Fluoroelastomers of Examples 3—6

Example	3	4	5	6
Composition	100	100	100	100
Polymer	25	30	30	30
MT Black				
Litharge (PbO)		3	3	3
Calcium Hydroxide	5			
TAIC ⁽⁴⁾		3	2.5	2.5
TMAIC ⁽⁵⁾				
Luperco 101-XL ⁽⁶⁾	3	5	5	5
Proton Sponge ⁽⁷⁾		0.5	0.5	0.5
TMS ⁽⁸⁾	0.8			
ODR, 30 min/177°C (ASTM D-2084)				
M _L , N.m 0.8	0.42	0.34	0.52	
M _H , N.m 4.5	5.63	4.28	5.83	
t ₉₀ , minutes	5.1	9.3	8.6	7.7
Stress/strain, press cured				
15 min/177°C and post-cured				
24 h/232°C (ASTM D-412)				
Original				
M ₁₀₀ , MPa	11.0	10.6	8.3	13.8
T _B , MPa	18.1	16.3	15.2	19.9
E _B , % 160	140	150	130	
Heat aged, Air oven, 70 h/275°C				
M ₁₀₀ , MPa	3.8	4.2	3.1	4.8
T _B , MPa	5.7	7.7	7.7	9.2
E _B , % 205	195	230	180	
Hardness, Shore A	75	81	75	79
% Compression Set (ASTM D-395, Method B)				
70 h/25°C	28	34	26	23
70 h/200°C	73	36	31	27
Clash-Berg, °C	-8			

(4) TAIC is triallyl isocyanurate

(5) TMAIC is trimethallyl isocyanurate

(6) 45% 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane and 55% inert filler

(7) 1,8-bis(dimethylamino)naphthalene

(8) TMS is tetramethylene sulfone

EP 0 208 314 B1

Example 7

A peroxide-curable fluoroelastomer was prepared as described in Example 1 except that the aqueous solution was fed at 1.20 L/h for a nominal residence time of 1.67h in the 2.0-liter reactor. Components of the aqueous solution were fed to the reactor at a rate of 3.0 g/h ammonium persulfate, 14.0 g/h disodium phosphate buffer, and 1.8 g/h ammonium perfluorooctanoate soap. Gaseous monomers were fed to the reactor at rates of 29 g/h ethylene, 146 g/h tetrafluoroethylene, and 200 g/h perfluoro(methyl vinyl ether). The cure-site monomer, 4-iodo-3,3,4,4-tetrafluorobutene-1 (ITFB), was fed to the reactor at a rate of 2.4 g/h in a 15 volume % solution in tertiary butyl alcohol. After an equilibration period of six hours, the effluent latex was collected for six hours. The unreacted offgas from the degasser amounted to 84 g/h and had a composition of 0.0% ethylene, 17.6% tetrafluoroethylene, and 82.4% perfluoro(methyl vinyl ether) by weight. The polymerization rate was 293 g/h at a conversion of 78%. The effluent latex had a pH of 5.5 and contained 20.3% solids.

The isolated fluoroelastomer had the following composition:

Monomer	Wt %	Mol %
Ethylene	11	35
Tetrafluoroethylene	42	39
Perfluoro(methyl vinyl ether)	47	26
ITFB	0.5	0.2

The inherent viscosity was 0.37 dL/g and the Mooney viscosity ML-10(100°C) was 16. The glass transition temperature was -12°C and crystallinity was negligible.

A curable fluoroelastomer composition was prepared by mixing the following ingredients on a two-roll rubber mill whose rolls were heated to about 30°C: 100 parts fluoroelastomer of Example 8, 30 parts MT carbon black, 3 parts lead oxide (litharge), 3 parts triallyl isocyanurate, and 3 parts "Luperco" 101-XL peroxide [45% of 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane and 55% inert filler]. The cure characteristics of the composition were measured with an oscillating disk rheometer (ODR) at a cure time of 30 minutes at 177°C, according to ASTM D-2084. The time required to reach 90% of the cure state reached in 12 minutes was determined as $t_{0.90}$ = 2.3 minutes. Test samples were press-cured for 30 minutes at 177°C and post-cured 18 hours at 204°C. Stress-strain properties were determined according to ASTM D-412 as: 100% modulus, M_{100} = 7.9 MPa; tensile at break, T_b = 9.0 MPa; elongation at break, E_b = 1300%.

Example 8

A fluoroelastomer was made as described in Examples 3-6 except that the aqueous solution was fed to a 4.0 liter reactor at a rate of 1.20 L/h for a nominal residence time of 3.3 h. Components of the aqueous solution were fed to the reactor at rates of 3.0 g/h ammonium persulfate, 13.0 g/h disodium phosphate buffer, and 2.7 g/h ammonium perfluorooctanoate soap. The gaseous monomers were fed to the reactor at rates of 21 g/h ethylene, 145 g/h tetrafluoroethylene, and 227 g/h perfluoro(methyl vinyl ether). The cure-site monomer, perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene) [8-CNVE] was fed to the reactor at a rate of 7.4 g/h. After an equilibration period of three hours at 80°C, the effluent latex was collected for six hours. The unreacted offgas amounted to 141 g/h and had a composition of 0% ethylene, 17% tetrafluoroethylene, and 83% perfluoro(methyl vinyl ether). The polymerization rate was about 256 g/h at a conversion of 64%.

The isolated fluoroelastomer had the following composition:

Monomer	Wt %	Mol %
Ethylene	8	28
Tetrafluoroethylene	47	46
Perfluoro(methyl vinyl ether)	43	25
8-CNVE	1.6	0.4

The polymer had a Mooney viscosity ML-10(100°C) of 72 and a glass transition temperature of -14°C with negligible crystallinity. The polymer containing 8-CNVE is curable using tetraphenyl tin as catalyst.

Example 9

A peroxide-curable fluoroelastomer was prepared as described in Example 1 with the following exceptions. The 4.0-liter reactor was filled with an aqueous solution of 2.0 g ammonium persulfate, 2.4 g ammonium perfluorooctanoate and 12.0 g disodium hydrogen phosphate heptahydrate buffer per liter of

EP 0 208 314 B1

deionized water at 79°C. An aqueous solution was introduced to the reactor at a rate of 0.50 L/h with components comprising 1.0 g/h ammonium persulfate, 6.0 g/h disodium phosphate buffer, and 1.2 g/h ammonium perfluorooctanoate soap. After one hour, monomers were added at rates of 8 g/h ethylene, 52 g/h tetrafluoroethylene, 73 g/h perfluoro(methyl vinyl ether), 25 g/h perfluoro(2-propoxy propyl vinyl ether) [PHVE], and 1.6 g/h 4-bromo-3,3,4,4-tetrafluorobutene-1 (BTFB). After an equilibration period of two hours, the effluent latex was collected for eight hours. After that time no further monomers were added and the latex remaining in the reactor was combined with that previously collected. The offgas during the last two hours amounted to 19 g/h and had a composition of 0% ethylene, 6% tetrafluoroethylene, and 94% perfluoro(methyl vinyl ether). The polymerization rate was approximately 124 g/h at a conversion of 77%.

The fluoroelastomer was isolated as described in Example 1.

The polymer had the following composition:

	Monomer	Wt %	Mol %
15	Ethylene	6	24
	Tetrafluoroethylene	41	44
	Perfluoro(methyl vinyl ether)	45	29
20	PHVE	7	2
	BTFB	1.2	0.6

The polymer had a Mooney viscosity ML-10 (100°C) of 15 and a glass transition temperature of -19°C, with negligible crystallinity.

Example 10

A continuous emulsion polymerization was carried out in a well-stirred 4 liter stainless steel reaction vessel. The reactor was filled with an aqueous solution containing 2.5 g ammonium persulfate (APS) initiator, 16.67 g disodium hydrogen phosphate heptahydrate buffer and 2.67 g ammonium perfluorooctanoate soap per liter of deionized water. The reactor was heated to 90°C and the aqueous solution was metered in at a rate of 1.20 l/h. The reactor was kept liquid-full at 6.3 MPa by means of a back-pressure control valve in the effluent line. After one hour the polymerization reaction was started by introducing a gaseous monomer mixture consisting of tetrafluoroethylene, perfluoromethyl perfluorovinyl ether and ethylene in a weight ratio of 42.8/52.3/4.9 which was fed through a diaphragm compressor at 462.3 g/h. After 0.5 hr, 4-bromo-3,3,4,4-tetrafluorobutene-1 was introduced at a rate of 6.2 g/h, metered as 7.6 ml/h of a 50 vol% solution in t-butanol.

The polymer latex effluent was separated from residual monomers in a degassing vessel at atmospheric pressure. Monomer offgas flow was measured at 113.0 g/h and had a composition of 0.01 weight % ethylene, 16.6 weight % tetrafluoroethylene and 83.4 weight % perfluoromethyl perfluorovinyl ether after the reactor had equilibrated for five hours. The tetrafluoroethylene-containing fluoroelastomer had the following composition:

TABLE V

	Monomer	wt %	Incorporated in Polymer Mole %
50	Ethylene	6.4	22.9
	Tetrafluoroethylene	50.5	51.0
	Perfluoromethyl perfluoro vinyl ether	41.5	25.3
55	4-bromo-3,3,4,4-tetrafluorobutene-1	1.6	0.8

The fluoroelastomer was isolated from the latex by reducing the pH to about 3 with dilute nitric acid and coagulating with a calcium nitrate solution. The coagulated polymer was allowed to settle and was washed by reslurrying in water twice and filtering. The wet crumb was dried in an air oven at 50-60°C to a moisture content of less than 1%.

Claims

1. A base resistant, substantially amorphous fluoroelastomer consisting of (1) 10-40 mole percent

EP 0 208 314 B1

ethylene units, (2) 32—60 mole percent tetrafluoroethylene units, (3) 20—40 mole percent perfluoro(alkyl vinyl ether) units wherein the alkyl group contains 1—5 carbon atoms and (4) a cure-site monomer.

2. A fluoroelastomer of Claim 1 wherein the perfluoro(alkyl vinyl ether) units are perfluoro(methyl vinyl ether).

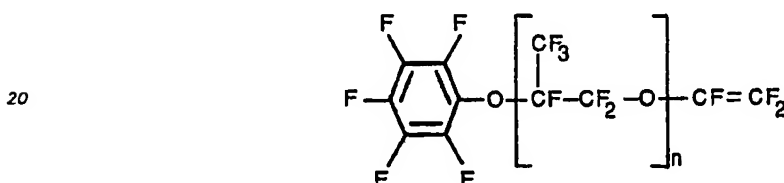
3. A fluoroelastomer of Claim 1 consisting of (1) 20—40 mole percent ethylene units, (2) 32—60 mole percent tetrafluoroethylene units, 20—30 mole percent perfluoro(alkyl vinyl ether) units and (4) a peroxide-curable cure-site monomer.

4. A fluoroelastomer of Claim 3 wherein the perfluoro(alkyl vinyl ether) units are perfluoro(methyl vinyl ether).

5. A fluoroelastomer of Claim 1 wherein the cure-site monomer is a bromine-containing olefin containing 2—20 carbon atoms.

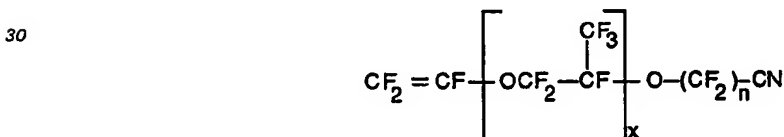
6. A fluoroelastomer of Claim 1 wherein the cure-site monomer is an iodine-containing olefin containing 2—20 carbon atoms.

7. A fluoroelastomer of Claim 1 wherein the cure-site monomer is a halogenated vinyl ether of the formula:



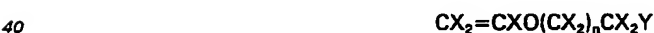
where n is 1 or 2,

8. A fluoroelastomer of Claim 1 wherein the cure-site monomer is a halogenated vinyl ether of the formula:



where X is 1 to 2, and n is 1 to 4.

9. A fluoroelastomer of Claim 1 wherein the cure-site monomer is a halogenated vinyl ether of the formula:



where Y is chlorine, bromine or iodine, X is hydrogen or fluorine and n is 1 to 9.

10. A fluoroelastomer of Claim 5 wherein the bromine-containing olefin is 4-bromo-3,3,4,4-tetrafluorobutene-1.

11. A fluoroelastomer of Claim 8 wherein the halogenated vinyl ether is perfluoro-(8-cyano-5-methyl-3,6-dioxa-1-octene).

12. A fluoroelastomer of Claim 5 containing a polyunsaturated compound that is a coagent and capable of cooperating with a peroxide curing agent.

13. A fluoroelastomer of Claim 12 wherein the polyunsaturated compound is trimethylallylisocyanurate or triallylisocyanurate.

Patentansprüche

1. Basenbeständiges, im wesentlichen amorphes Fluoroelastomer, bestehend aus
 - (1) 10 bis 40 Mol-% Ethylen-Einheiten,
 - (2) 32 bis 60 Mol-% Tetrafluoroethyleinheiten,
 - (3) 20 bis 40 Mol-% Perfluoro(alkylvinylether)Einheiten, worin die Alkyl-Gruppe 1 bis 5 Kohlenstoff-Atome enthält, und
 - (4) ein Härtungszentren-Monomer.
2. Fluoroelastomer nach Anspruch 1, worin die Perfluoro(alkylvinylether)-Einheiten Perfluoro(methylvinylether) sind.
3. Fluoroelastomer nach Anspruch 1, bestehend aus
 - (1) 20 bis 40 Mol-% Ethylen-Einheiten,
 - (2) 32 bis 60 Mol-% Tetrafluoroethyleinheiten,
 - (3) 20 bis 35 Mol-% Perfluoro(alkylvinylether)Einheiten, und

EP 0 208 314 B1

(4) einem mit Peroxid härtbaren Härtungszentren-Monomer.

4. Fluoroelastomer nach Anspruch 3, worin die Perfluoro(alkylvinylether)-Einheiten Perfluoro(methylvinylether) sind.

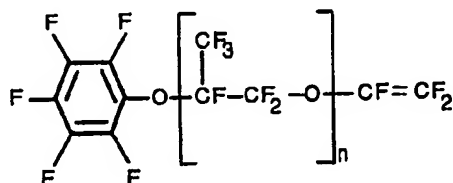
5. Fluoroelastomer nach Anspruch 1, worin das Härtungszentren-Monomer ein bromhaltiges Olefin mit 2 bis 20 Kohlenstoff-Atomen ist.

6. Fluoroelastomer nach Anspruch 1, worin das Härtungszentren-Monomer ein iodhaltiges Olefin mit 2 bis 20 Kohlenstoff-Atomen ist.

7. Fluoroelastomer nach Anspruch 1, worin das Härtungszentren-Monomer ein halogenierter Vinylether der Formel

10

15

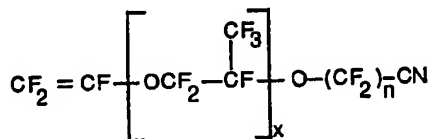


ist, in der n 1 oder 2 ist.

20

8. Fluoroelastomer nach Anspruch 1, worin das Härtungszentren-Monomer ein halogenierter Vinylether der Formel

25



ist, in der x 1 bis 2 ist und n 1 bis 4 ist.

30

9. Fluoroelastomer nach Anspruch 1, worin das Härtungszentren-Monomer ein halogenierter Vinylether der Formel



35

ist, in der Y Chlor, Brom oder Iod ist, X Wasserstoff oder Fluor ist und n 1 bis 9 ist.

10. Fluoroelastomer nach Anspruch 5, worin das bromhaltige Olefin 4-Bromo-3,3,4,4-tetrafluorobuten-1 ist.

11. Fluoroelastomer nach Anspruch 8, worin der halogenierte Vinylether Perfluoro-(8-cyano-5-methyl-3,6-dioxa-1-octen) ist.

40

12. Fluoroelastomer nach Anspruch 5, enthaltend eine polyungesättigte Verbindung, die ein Co-Agens ist und befähigt ist, mit einem Peroxid-Härtungsmittel zusammenzuwirken.

13. Fluoroelastomer nach Anspruch 12, worin die polyungesättigte Verbindung Trimethallylisocyanurate oder Triallylisocyanurat ist.

45

Revendications

1. Un fluoroélastomère pratiquement amorphe, résistant aux bases, comprenant:

(1) 10 à 40% en moles de motifs éthyléniques;

(2) 32 à 60% en moles de motifs tétrafluoroéthyléniques;

50

(3) 20 à 40% en moles de motifs perfluoro(alkylvinyléthers), dans lesquels le groupe alkyle contient de 1 à 5 atomes de carbone; et

(4) un monomère de durcissement ou vulcanisation.

2. Un fluoroélastomère selon la revendication 1, dans lequel les motifs perfluoro(alkylvinyléthers) sont des motifs perfluoro(méthylvinyléthers).

55

3. Un fluoroélastomère selon la revendication 1, comprenant:

(1) 20 à 40% en moles de motifs éthyléniques;

(2) 32 à 60% en moles de motifs tétrafluoroéthyléniques;

(3) 20 à 35% en moles de motifs perfluoro(alkyl-vinyléthers); et

(4) un monomère de durcissement, durcissable sous l'effet d'un peroxyde.

60

4. Un fluoroélastomère selon la revendication 3, dans lequel les motifs perfluoro(alkylvinyléthers) sont des motifs perfluoro(méthylvinyléthers).

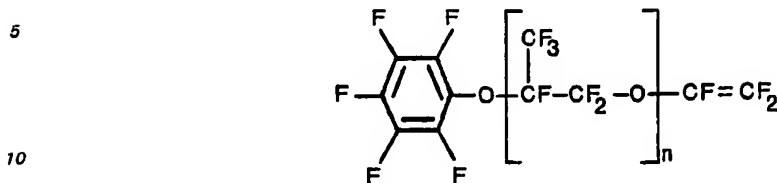
5. Un fluoroélastomère selon la revendication 1, dans lequel le monomère de durcissement est une oléfine bromée contenant 2 à 20 atomes de carbone.

6. Un fluoroélastomère selon la revendication 1, dans lequel le monomère de durcissement est une oléfine iodée contenant 2 à 20 atomes de carbone.

65

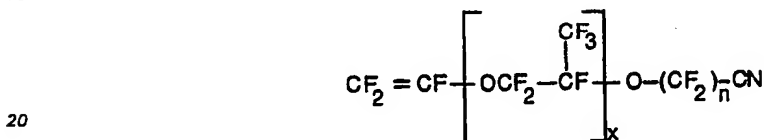
EP 0 208 314 B1

7. Un fluoroélastomère selon la revendication 1, dans lequel le monomère de durcissement comporte un vinyléther halogéné de formule:



dans laquelle n vaut 1 ou 2.

8. Un fluoroélastomère selon la revendication 1, dans lequel le monomère de durcissement est un vinyléther halogéné de formule:



dans laquelle:

X vaut 1 à 2; et

n vaut 1 à 4.

9. Un fluoroélastomère selon la revendication 1, dans lequel le monomère de durcissement est un vinyléther halogéné de formule:



dans laquelle:

Y est le chlore, le brome ou l'iode;

X est un atome d'hydrogène ou de fluor; et

n vaut 1 à 9.

10. Un fluoroélastomère selon la revendication 5, dans lequel l'oléfine bromée est le 4-bromo-3,3,4,4-tétrafluorobutène-1.

11. Un fluoroélastomère selon la revendication 8, dans lequel le vinyléther halogéné est le perfluoro-(8-cyano-5-méthyl-3,6-dioxa-1-octène).

12. Un fluoroélastomère selon la revendication 5, contenant un composé poly-insaturé qui est un co-agent et est capable de coopérer avec un agent de durcissement du type peroxyde.

13. Un fluoroélastomère selon la revendication 12, dans lequel le composé poly-insaturé est l'isocyanurate de triméthallyle ou l'isocyanurate de triallyle.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☒ FADED TEXT OR DRAWING

☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☒ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.